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MOST PREFERRED EMBODIMENT TO CARYOUT THE INVENTION

In the method of the present invention, the process in which a insulating film is formed is not clear. However, it is considered that a perfluorocycloolefin is decomposed and concurrently polymerized by ring-opening or addition reaction.

In the present invention, the term "the material gas comprising a perfluorocycloolefin as the main component" means a material gas in which the reactive component is substantially the perfluorocycloolefin alone or a material gas comprising perfluorocycloolefin and a minor portion (usually 30% by weight or less) of linear perfluoroclefin. Into the material gas, dilution gases may be mixed in order to control the reactivity and to improve handling performance. Examples of the dilution gas include rare gases and gases of hydrocarbons. Examples of the rare gas include argon, helium and xenon. As the gases of hydrocarbons, gases of hydrocarbons having 1 to 3 carbon atoms are usually used. Examples of gases of hydrocarbons include methane, ethylene and acetylene. Preferred dilution gases are argon, methane and ethylene. These dilution gases can be used singly or in combination of two or more dilution gases. The content of the dilution gas is usually 95% by weight or less based on the total amount of the reactive component and the dilution gas.

The perfluorocycloolefin is not particularly limited. Usually, perfluorocycloolefins having a carbon atom of 3 to 8, preferably 4 to 6 and more preferably 5 are used. Examples of such perfluorocycloolefin include perfluorocyclopropene, perfluorocyclobutene, perfluorocyclopentene, perfluorocyclohexene, perfluorocyclohexene, perfluorocyclohexene, perfluorocyclohexene, perfluorocyclooctene, perfl

(1-methylcyclobutene), perfluoro(3-methylcyclobutene), perfluoro-(1-methylcyclopentene) and perfluoro(3-methylcyclopentene). Among these compounds, perfluorocycloolefins such as perfluorocyclobutene, perfluorocyclopentene and perfluorocyclohexene are preferable, and perfluorocyclopentene is most preferable. The perfluorocycloolefin may be used singly or in combination of two or more types.

In the present invention, other perfluoroolefin than perfluorocycloolefin, namely, linear unsaturated perfluorocarbons can be used together with the perfluorocyclolefin. However, when these other perfluoroolefins are used in great amount, the object of the present invention cannot be attained. The amount of other perfluoroolefins is usually 30% by weight or less, preferably 20% by weight or less and more preferably 10% by weight or less based on the total amount of the fluorocarbons.

As the procedures in the plasma CVD process, conventionally known procedures described, for example, in Japanese Patent Application Laid-Open No. Heisei 9(1997)-237783 can be adopted. The conditions for forming plasma usually used are: output of radio frequency (RF) of 10 W to 10 kW, temperature of an article to be treated of 0 to 500°C and pressure of 0.1 mmTorr to 100 Torr. The thickness of the formed film is, in general, in the range of 0.01 to 10 μ m.

As the apparatus used for the plasma CVD, in general, CVD apparatuses of the parallel flat plate type are used. Microwave CVD apparatuses, ECR-CVD apparatuses and high density plasma (such as helicon wave plasma and inductivity coupled plasma) CVD apparatuses can also be used.

Irradiation with ultraviolet light from a low pressure mercury lamp may be conducted to promote dissociation of the material gas and decrease

damages on the article to be treated. The article to be treated and the space of the reaction may be irradiated with ultrasonic wave to promote migration of the perfluorocycloolefin.

The process of forming the insulating film from a perfluorocycloolefin on a semiconductor substrate to be treated in accordance with the CVD process of the present invention will be described more specifically with reference to examples in the following.

Example 1

The plasma CVD of an insulating film was conducted using, as the plasma CVD apparatus, a plasma CVD apparatus of the parallel flat plate type under the conditions as described below using, as a substrate, an oxidized silicon film wafer on a portion of which aluminum was deposited.

Perfluorocyclopentene (C₅F₈): 40 sccm

Argon: 400 sccm

Pressure: 250 mmTorr.

RF output (the frequency: 13.56 MHz): 400 W

Temperature of the substrate: 260°C

A film having a thickness of 0.5 µm was obtained after treatment under the condition set forth above. The obtained film was dense and uniform and exhibited a good adhesiveness to the substrate. No voids were found on the obtained film. The relative dielectric constant of the film was 2.4.

Example 2

The plasma CVD of an insulating film was conducted using, as the plasma CVD apparatus, a plasma CVD apparatus of the parallel flat plate type under the conditions as described below using, as a substrate, an oxidized silicon film wafer on a portion of which aluminum was deposited.

Perfluorocyclobutene (C_4F_8): 40 sccm

Argon: 400 sccm

Pressure: 250 mmTorr.

RF output (the frequency: 13.56 MHz): 400 W

Temperature of the substrate: 260°C

A film having a thickness of $0.5~\mu m$ was obtained after treatment under the condition set forth above. The obtained film was dense and uniform and exhibited a good adhesiveness to the substrate. No voids were found on the obtained film. The relative dielectric constant of the film was 2.5.

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INDUSTRIAL APPLICABILITY

A dense and uniform insulating film having low dielectric constant can be obtained in accordance with the method of the present invention by forming an insulating film from perfluorocycloolefin by plasma CVD process. It is considered that the insulating film is formed by ring-opening or addition polymerization of the perfluorocycloolefin under the condition of plasma treatment. The method has an industrial advantage in that the handling of the material gas is easy and that it is not necessary to mix methane, hydrogen and nitriding agent gases such as N_2 , NH_3 or N_2H_4 into the material gas.

The process of forming the insulating film in accordance with the plasma CVD process of the present invention is applicable to forming inter-layer insulating film or other insulating material layers on an aluminum based metal wiring or forming final passivation films in the

manufacturing processes of semiconductor devices.

Furthermore, the process is also applicable to forming insulating films of glass substrate and insulating film after transistors are formed in manufacturing processes of TFT displays, forming insulating films when and after pixels are formed in manufacturing processes of CCD used for solid image sensor, forming insulating films on the electronic elements such as metal wiring of copper or aluminum and condensers formed on substrates in manufacturing processes of fine printed plates or micro chip modules, forming insulating films on metal wirings of copper, nickel and aluminum and sliding members composed of metal electrically conductive materials in manufacturing processes of precision connectors, precision switches and precision motors, and forming insulating films on electrode metals such as aluminum and sliding members composed of electrically conductive materials of metals in manufacturing processes of precision condensers.

Still furthermore, the plasma CVD process of the present invention can be applicable to forming anti-reflection films on the surfaces of panels of color Braun tubes or Braun tubes for displays.